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The Entropies of Some Aqueous Ions

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Since the publication of the excellent summary of the entropies of aqueous ions by Latimer, Pitzer and Smith,[1] new data have become available which make possible an extension and revision of some of their values. The standard state for ionic entropies and the theoretical and practical importance of the results have been discussed in their papers.

Entropy of Dihydrogen Phosphate Ion.—For the reaction $KH_2PO_4 = K^+ + H_2PO_4^-$, $\Delta H^0 = 4697$ cal.[2] at 296.1°K. The correction to 298.1°K. is small enough to be ignored. The activity coefficient of the saturated solution, 1.85 *m*, is 0.315 from an extrapolation of unpublished results of G. Scatchard and R. G. Breckenridge. $\Delta F^0_{298\cdot1} = -RT \ln (\gamma m)^2 = 640$ cal., and hence $\Delta S^0_{298\cdot1} = 13.6$. The entropies of KH_2PO_4[3] and $K^{+(1)}$ are 32.23 ± 0.1 and 24.2 ± 0.2 cal. deg.$^{-1}$ mole^{-1}; therefore, the entropy of the dihydrogen phosphate ion is 21.6 ± 0.3 cal. deg.$^{-1}$ mole^{-1}.

The value for this ion given by Latimer, Pitzer and Smith is 28 ± 1.5; their calculations for the entropies of $PO_4^{\equiv}$, $HPO_4^=$, $H_2PO_4^-$ and H_3PO_4 involve the measured solubility product of lead phosphate, the entropy of the lead ion, and the ionization constants as well as the necessary thermal data. Their value for the dihydrogen phosphate ion can be given no weight in comparison to the value obtained above, in view of the possibilities of error in the numerous experimental data from various sources used in their calculations. The entropies of the other substances will be recalculated.

Entropy of $HPO_4^=$, $PO_4^{\equiv}$ and H_3PO_4.—The best values for these substances are derived from $S^0_{H_2PO_4^-} = 21.6$ and the following equations, the $\Delta S^0_{298\cdot1}$ values being those given in Ref. 1.

$$H_2PO_4^- = H^+ + HPO_4^= \qquad \Delta S^0 = -30.3 \quad S^0_{HPO_4^=} = -8.7 \pm 1.0$$

$$HPO_4^= = H^+ + PO_4^{\equiv} \qquad \Delta S^0 = -43 \quad S^0_{PO_4^{\equiv}} = -52 \pm 2$$

$$H_3PO_4 = H^+ + H_2PO_4^- \qquad \Delta S^0 = -16.0 \quad S^0_{H_3PO_4} = 37.6 \pm 1.0$$

These values are recommended in place of those given in Ref. 1.

From measurements of the ionization constant of the dihydrogen phosphate ion as a function of the temperature, Bates and Acree[4] have found $\Delta S^0 = -29.6$; the value given above is preferred because a calorimetric determination of the heat of reaction was used.

Entropy of Ammonium Ion.—The activity coefficient of a saturated solution, 3.57 *m*, of ammonium dihydrogen phosphate is estimated to be 0.185 by assuming that the activity coefficients are equal to those of the corresponding potassium salt. This estimate involves an extrapolation of the measured activity coefficients, but neither the extrapolation nor the assumption that the activity coefficients of the ammonium and potassium salts are equal is likely to introduce an error of more than 0.3 entropy unit in the entropy of the ammonium ion.

For the reaction $NH_4H_2PO_4 = NH_4^+ + H_2PO_4^-$, $\Delta F^0_{298\cdot1} = 492$ cal. and $\Delta H^0 = 3928$ cal.[2]; therefore, $\Delta S^0_{298\cdot1} = 11.5$. The entropy of $NH_4H_2PO_4$ is 36.32 ± 0.1[5] and, with the entropy of the dihydrogen phosphate ion given above, 26.2 is obtained for the entropy of the ammonium ion. This is in good agreement with the values 26.5 based on the entropy of ammonia and its dissociation constant, and 27.1 derived from the solubility product and entropy of ammonium chloride. The value 26.6 ± 0.5 cal. deg.$^{-1}$ mole^{-1} is recommended for the entropy of the ammonium ion.

Entropy of Dihydrogen Arsenate Ion.—The entropies of potassium dihydrogen arsenate[6] and ammonium dihydrogen arsenate[7] are 37.08 ± 0.1 and 41.12 ± 0.1 cal. mole^{-1} deg.$^{-1}$, respectively. The activity coefficient of a saturated solution of KH_2AsO_4, 1.42 *m*, at 25° is 0.41 from an extrapolation of the unpublished measurement of G. Scatchard and R. G. Breckenridge. For the saturated solution, 3.29 *m*, of the ammonium salt, the activity coefficient is estimated to be 0.30. Unfortunately the heats of solution of these two salts are not known with accuracy, but if the approximate data available are used, the following values are obtained for the entropy of the dihydrogen arsenate ion

$$KH_2AsO_4 = K^+ + H_2AsO_4^- \qquad \Delta F^0_{298\cdot1} \doteq 640 \quad \Delta H^0 = 4800^8 \quad S^0_{H_2AsO_4^-} = 26.8$$

$$NH_4H_2AsO_4 = NH_4^+ + H_2AsO_4^- \qquad \Delta F^0_{298\cdot1} = 14 \quad \Delta H^0 = 4250^9 \quad S^0_{H_2AsO_4^-} = 28.7$$

A provisional value for the entropy of the dihydrogen arsenate ion is taken as 28 ± 1.0 cal. deg.$^{-1}$ mole^{-1}.

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(1) W. M. Latimer, K. S. Pitzer and W. V. Smith, THIS JOURNAL, **60**, 1829 (1938).

(2) K. Chomjakow, A. Jaworowskaja and P. Schirokich, *Z. physik. Chem.*, **A167**, 38 (1933).

(3) C. C. Stephenson and J. G. Hooley, THIS JOURNAL, **66**, 1397 (1944).

(4) R. G. Bates and S. F. Acree, *Natl. Bur. Standards*, **30**, 129 (1943).

(5) C. C. Stephenson and A. C. Zettlemoyer, THIS JOURNAL, **66**, 1402 (1944).

(6) C. C. Stephenson and A. C. Zettlemoyer, *ibid.*, **66**, 1405 (1944).

(7) C. C. Stephenson and H. E. Adams, *ibid.*, **66**, 1409 (1944).

(8) Bichowsky and Rossini, "Thermochemistry of Chemical Substances," Reinhold Publishing Corporation, New York, N. Y., 1936.

(9) A. de Passillé, *Ann. chim.*, **11**, 5, 107 (1936).

Entropy of Sulfate Ion.—Five independent paths are given in ref. 1 for determining the entropy of the sulfate ion, and from the most accurate of these, which involves the entropy of sodium sulfate decahydrate, 4.4 ± 1 cal. deg.$^{-1}$ mole^{-1} was selected. From more recent data, two additional calculations of higher accuracy are possible. The reactions, and the data pertaining to them, are summarized below.

The entropies of sodium sulfate,[10] potassium sulfate,[11] and the sodium ion[1] are 35.7 ± 0.1, 42.0 ± 0.6 and 14.0 ± 0.4 cal. deg.$^{-1}$ mole^{-1}. $K_2SO_4 = 2K^+ + SO_4^=$, $\Delta F^0_{298\cdot1} = 2420$,[12] $\Delta H^0_{298\cdot1} = 5680$,[13] $S^0_{SO_4^=} = 4.5 \pm 0.8$. $Na_2SO_4 = 2Na^+ + SO_4^=$, $\Delta F^0_{298\cdot1} = 435$[12], $\Delta H^0_{208\cdot1} = -560$[10], $S^0_{SO_4^=} = 4.4 \pm 0.5$. The excellent agreement with the value from ref. 1 serves as additional evidence for the zero-point entropy of sodium sulfate decahydrate postulated by Pitzer and Coulter.[10] The value 4.4 ± 0.5 will be used.

Entropy of Calcium Ion.—With the entropy of the sulfate ion established above, and the unusually complete thermodynamic data concerning $CaSO_4\cdot2H_2O$ and $CaSO_4$ (anhydrite), a reliable value for the entropy of the calcium ion may be obtained. The entropies[14] of $CaSO_4\cdot2H_2O$ and anhydrite are 46.4 ± 0.2 and 25.5 ± 0.4 cal. deg.$^{-1}$ mole^{-1}. For the reaction

$$CaSO_4\cdot2H_2O = CaSO_4 \text{ (anhydrite)} + 2H_2O \text{ (liq.)}$$

three concordant values of 4030,[14] 3990[15] and 3970 cal.[16] have been given for $\Delta H^0_{298\cdot1}$. Using the average, 4000 cal., and $\Delta S^0 = 12.6$ from third law measurements, one finds $\Delta F^0_{298\cdot1} = 240$ cal. At 315.1°K. the solubilities of the two salts are equal and $\Delta F^0_{315\cdot1} = 0$ since the activity of the water in this dilute solution may be taken as one without appreciable error. From this value and from ΔH^0 and ΔC_p for the reaction, $\Delta F^0_{298\cdot1} = 230$ cal. The agreement between this value and that calculated from thermal data alone removes any doubt concerning the possibility of a zero-point entropy for $CaSO_4\cdot2H_2O$ similar to that for $Na_2SO_4\cdot10H_2O$.

The above reaction may now be considered as the difference between the two reactions $CaSO_4\cdot2H_2O = Ca^{++} + SO_4^= + 2H_2O$ and $CaSO_4 = Ca^{++} + SO_4^=$. The difference between the free energy changes of the two reactions must be 230 cal. The solubilities of $CaSO_4\cdot2H_2O$ and $CaSO_4$ (anhydrite) at 25° are 0.0153 *m* and 0.0204 *m*, respectively. However, there are no reliable experimental values for the activity coefficients of the saturated solutions, but these may be deduced from the fact that the activity coefficients in these dilute solutions can certainly be expressed by an equation of the form $\log \gamma = -0.2034\cdot\mu^{1/2}/(1 + A\mu^{1/2})$. If A is simply taken as one, the standard free energy of solution of $CaSO_4\cdot2H_2O$ is 6050 cal. and for anhydrite the free energy of solution is 5840 cal.; the difference of 210 cal. agrees satisfactorily with that given above. The limiting Debye–Hückel law gives a smaller difference of 130 cal.

The entropy calculation may now be summarized. For the solution of $CaSO_4\cdot2H_2O$

$$\Delta F^0 = 6050 \qquad \Delta H^0 = -270^{17} \qquad S^0_{Ca^{++}} = -12.7$$

For the solution of $CaSO_4$

$$\Delta F^0 = 5840 \qquad \Delta H^0 = -4270 \qquad S^0_{Ca^{++}} = -12.8$$

Latimer, Pitzer and Smith have given $S^0_{Ca^{++}} = -11.4 \pm 0.3$. Their value, which was derived from the reaction

$$CaCO_3 + 2H^+ = Ca^{++} + H_2O(l) + CO_2(g)$$

is certainly not as accurate as their estimate and probably does not represent a serious disagreement with the values just derived. Because the data for the $CaSO_4$ system are quite consistent, −12.7 ± 0.6 cal. deg.$^{-1}$ mole^{-1} is recommended for the entropy of the calcium ion.

In Table I are assembled the entropy data for the above substances.

TABLE I

STANDARD ENTROPIES AT 298.1°K.

Substance	Cal. deg.$^{-1}$ mole^{-1}	Substance	Cal. deg.$^{-1}$ mole^{-1}
$H_2PO_4^-$	21.6 ± 0.3	NH_4^+	26.6 ± 0.5
$HPO_4^=$	−8.7 ± 1.0	$H_2AsO_4^-$	28 ± 1.0
$PO_4^{\equiv}$	−52 ± 2	$SO_4^=$	4.4 ± 0.5
H_3PO_4	37.6 ± 1.0	Ca^{++}	−12.7 ± 0.6

Summary

The standard entropies at 298.1°K. have been calculated for the following substances: $H_2PO_4^-$, $HPO_4^=$, $PO_4^{\equiv}$, H_3PO_4, NH_4^+, $H_2AsO_4^-$, $SO_4^=$ and Ca^{++}.

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(10) K. S. Pitzer and L. V. Coulter, THIS JOURNAL, **60**, 1310 (1938).

(11) G. E. Moore and K. K. Kelley, *ibid.*, **64**, 2949 (1942).

(12) R. A. Robinson, J. M. Wilson and R. H. Stokes, *ibid.*, **63**, 1011 (1941).

(13) K. P. Mischtschenko and M. S. Pronina, *Zurnal obščej Chim.* (*Russ.*), **6**, 95 (1936).

(14) W. M. Latimer, J. F. G. Hicks and P. W. Schutz, *J. Chem. Phys.*, **1**, 424 (1933); K. K. Kelley, J. C. Southard and C. T. Anderson, *U. S. Bur. Mines, Tech. Paper*, **625** (1941).

(15) E. S. Newman and L. S. Wells, *J. Research Natl. Bur. Standards*, **20**, 825 (1938).

(16) E. A. Gulbransen, quoted by K. K. Kelley, U. S. Bur. Mines, Bull., 406 (1937).

(17) E. Lange and J. Monheim, *Z. physik. Chem.*, **150A**, 349 (1930).